

Synergistic Catalytic Cracking Mechanism of COCH_4 on Ni (111) Surface

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Abstract: In this paper, the mechanism of significant synergism between CO and CH_4 in Ni catalytic cracking is studied by theoretical calculation. The results show that the first and last H dissociation step is the rate control step in the step-by-step cracking of CH_4 . CO is directly decomposed into C and O on Ni (111) surface. In the process of CO/CH_4 catalytic cracking, the product O of CO cracking can change the pathway of the last step of CH_4 cracking, and the reaction energy barrier of this step is lower than that of CH direct cracking. The reaction energy barrier of CH_4 pyrolysis product H is lower than that of CO direct pyrolysis reaction. The intermediate product OH can change the last step of CH_4 pyrolysis. The step is that the reaction energy barrier of CH_4 pyrolysis is lower than that of CH direct pyrolysis reaction.

1. Introduction

The main component of natural gas is methane (CH_4), which contains almost no impurities such as sulfur and ash. It is a clean and environmentally friendly energy source. Natural gas is abundant in the world, and there are still a lot of resources in the seabed that have not been exploited. Compared with direct combustion, catalytic cracking to produce hydrogen (H_2) and carbon nanotubes (CNTs) is a new way to utilize natural gas. This method can not only prepare high performance carbon materials but also avoid carbon dioxide (CO_2) emissions. The H_2 produced by this method is a cleaner secondary energy source. It can also be used as chemical raw materials. It has a good application prospect. The pyrolysis temperature of CH_4 without catalyst is above 1000 C. The catalyst can effectively reduce the pyrolysis temperature of methane. Nickel (Ni) atom is a common catalyst in catalytic cracking of CH_4 because of its high d-electron orbital characteristic number, high catalytic activity and good CH_4 selectivity, which can reduce the catalytic temperature to about 500 C. At the same time, nickel ore has abundant reserves and relatively low price, so catalytic cracking of CH_4 with Ni has a good application prospect.

2. Calculation method and geometric configuration

2.1 Computing method

The functional form is generalized gradient approximation GGA-PBE. The pseudopotential uses Vanderbilt super-soft pseudopotential. The transition state search method is LST/QST (complete linear synchronous transit/quadratic synchronous transit). The cut-off point of kinetic energy of plane wave base group is 400 eV and k-point is $4 \times 4 \times 1$. The convergence accuracy of self-consistent field calculation is 1.0×10^{-5} eV/atom, the stress on each atom is less than 0.03 eV/Å, the tolerance offset is less than 0.001 Å and the stress deviation is less than 0.05 GPa.

Adsorption energy E_{ad} is defined as the change of total energy of the system before and after adsorption, as shown in equation (1):

$$E_{\text{ad}} = E_{\text{adsorbat}} + E_{\text{Ni}(111)} - E_{\text{adsorbat+Ni}(111)}, \quad (1)$$

In the formula (1), E_{adsorbat} is the adsorbate energy. $E_{\text{Ni}(111)}$ is the surface energy of Ni (111) adsorption. $E_{\text{adsorbat+Ni}(111)}$ is the total energy of the system after adsorption on Ni (111) surface.

The charge density difference Δq is defined as the change of charge density before and after adsorption, as shown in equation (2):

$$\Delta q = q_{\text{adsorbat}} + q_{\text{Ni(111)}} - q_{\text{adsorbat+Ni(111)}}, \quad (2)$$

In the formula (2), q_{adsorbat} is the charge density distribution of the adsorbate. $q_{\text{Ni(111)}}$ is the charge density distribution on the surface of Ni (111) adsorption. $q_{\text{adsorbat + Ni(111)}}$ is the charge density distribution of the system after adsorption on Ni (111) surface.

Energy barrier E is defined as the energy change from reactant to transition state, as shown in equation (3):

$$E_b = E_{\text{TS}} - E_{\text{IS}}, \quad (3)$$

In the formula (3), E_{TS} is the transition state energy and E_{IS} is the initial state energy.

2.2 Geometric configurations of Ni (111), CO and CH₄

Ni (111), Ni (110) and Ni (100) planes are the three main crystal planes of Ni crystals. Among them, the surface energy and free enthalpy of Ni (111) are the lowest, and are considered to be the most stable and catalytic surface, which is also the catalytic cracking surface studied in this paper. The original cell parameters of Ni are derived from AMCSD database.

There are four highly symmetrical adsorption sites on the surface of Ni (111): Top, Bridge, Hcp and Fcc, as shown in figure.1 (a). The configurations of CO molecule and CH₄ molecule are shown in figure.1 (b) and (c), respectively, in which CH₄ molecule is tetrahedral.

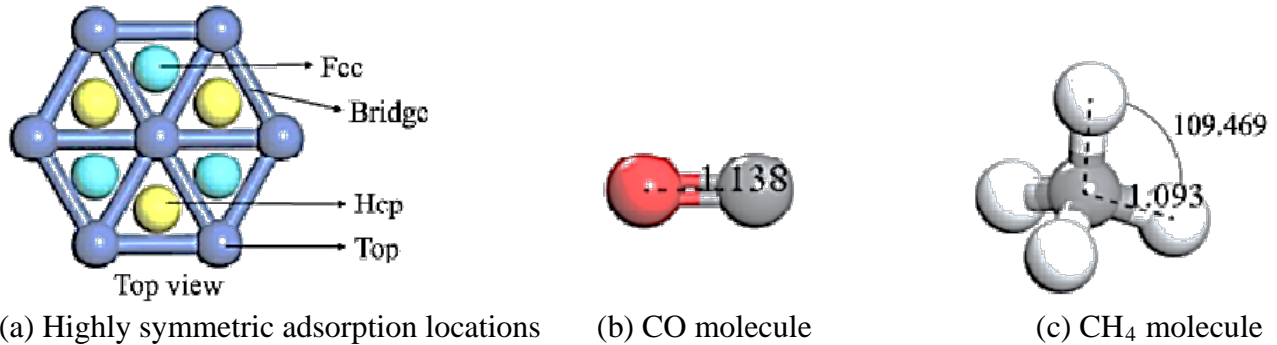


Figure 1 Catalytic surface and pyrolysis molecule

3. Results analysis

The calculation results show that CO cannot directly combine with CH_n (n = 4, 3, 2, 1) to produce intermediate products, while the intermediate products can combine with CO and CH_n. Therefore, the synergistic catalytic cracking mechanism is developed from three aspects: CO, CH₄ and OH produced in the intermediate process.

3.1 Effect of CO cracking product O on CH₄ catalytic cracking

The adsorption energy of CH₄ at each adsorption site is less than 40 kJ/mol, so it is physical adsorption, and the most stable adsorption site is Bridge site. The most stable adsorption sites of CH₃, CH₂, CH and C are Fcc sites, which are all chemical adsorption. The adsorption energies are 249, 480, 409 and 774 kJ/mol, respectively. It can be seen that the initial adsorption capacity of CH₄ on the surface of catalyst is poor, but once cracking occurs, it can be chemically adsorbed on the surface.

CH₄ is stable and does not bind to O as intermediate product. CH₃, CH₂ and CH can bind to O and then crack to H or OH. Before binding, the most stable adsorption sites of O are Fcc sites, and the most stable adsorption sites of CH_n (n = 3, 2, 1) are Fcc sites closest to O.

Oxygen produced by CO pyrolysis can promote CH₄ pyrolysis. The mechanism is that the energy barrier of CH pyrolysis in the last step of CH₄ pyrolysis is higher, so CH is easy to combine with O produced by CO pyrolysis to form CHO, and then decompose into C and OH. The energy barrier of this pathway is lower, which is more conducive to the formation of C.

3.2 Effect of CH₄ cracking product H on CO catalytic cracking

There are two possibilities for CO single component catalytic cracking pathway. The calculation results show that the most stable adsorption form of CO on Ni (111) is that CO is adsorbed at the Hcp site on the vertical surface under the direction of C, which is chemical adsorption. The transition state of the first path is not found in the calculation attempt, but the second path exists. When H exists, CO binds with it to form COH, and then cracks to produce C and OH.

Firstly, O and CO are adsorbed at the adjacent Fcc sites respectively, and CO is a vertical adsorption form with C-end facing down. Then, H and CO are transferred to the HCP sites between the Fcc sites to form COH. Finally, OH in COH is transferred to the Fcc bit occupied by the original H, and C is transferred to the Fcc bit above the Hcp bit. H produced by CH₄ pyrolysis can promote CO pyrolysis. The mechanism is that the energy barrier of CO direct pyrolysis is high, so CO can easily combine with H to form COH, and then decompose into C+OH. The energy barrier of this pathway is lower, which is more conducive to the generation of C.

3.3 Effect of cleavage intermediate OH on catalytic cracking of CH₄

CH₄ pyrolysis product H participates in CO pyrolysis and produces OH. OH is also formed after CO pyrolysis product O participates in CH₄ pyrolysis. Therefore, OH may also participate in the catalytic cracking process. The possibility of CO, CH₄ and OH binding was not found in the calculation attempt, but CH₃, CH₂ and CH could be combined with OH, and OH grabbed one H to generate hydrogen peroxide.

Firstly, O in OH is bound to H in CH_n, which leads to the activation of C-H, the increase of bond length and the formation of intermediate product CH_nOH. As shown in Table 1, the energy barrier is smaller in the process of combining OH with CH_n and the cracking of its intermediate products to produce hydrogen peroxide. The combination of CH₃ and CH₂ with OH is less likely to regenerate hydrogen peroxide. The energy barrier of CH direct catalytic cracking is higher, so it can combine with OH to produce hydrogen peroxide.

Table 1 Energy changes in catalytic cracking of CH_n + OH

Reaction	Energy Barrier/(kJ/mol)	Reaction heat/(kJ/mol)
CH ₃ OH→CH ₂ +H ₂ O	64	-120
CH ₂ OH→CH+H ₂ O	50	-131
CHOH→C+H ₂ O	29	-153
CH ₂ +OH→CH ₂ OH	70	-15
CH ₃ +OH→CH ₃ OH	77	24
CH+OH→CHOH	56	-49

OH produced by CO/CH₄ synergistic pyrolysis can promote CH₄ pyrolysis. The mechanism is that the final energy barrier of CH₄ direct pyrolysis is high, so CHOH is easy to combine with OH to form CHOH, and then decompose into C+H₂O. This path has lower energy barrier and is more conducive to the formation of C.

4. Conclusions

The mechanism of co-catalytic cracking of CO and CH₄ on Ni (111) surface has three paths: the first path is that the energy barrier of CH cracking in the last step of CH₄ cracking is higher, so CH can easily combine with O produced by CO cracking to form CHO, and then crack into C and OH. The energy barrier of this path is lower, which is more conducive to the formation of C. The second path is the high energy barrier of CO direct pyrolysis, so CO is easy to combine with H to produce COH, and then decompose into C+OH. This path has lower energy barrier and is more conducive to the generation of C. The third path is the high potential barrier of the last step in direct cracking of CH₄. Therefore, CH is easy to combine with OH produced by C O/CH₄ co-cracking to form CHOH,

and then decompose into C+H₂O. The energy barrier of this path is lower, which is more conducive to the formation of C.

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